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COMPLETE SPECIFICATION

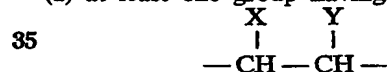
Preparation of Aliphatic Carboxylic Acids

We, ROHM & HAAS COMPANY, a Corporation organized under the laws of the State of Delaware, United States of America, of 222, West Washington Square, Philadelphia 5, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in 10 and by the following statement:—

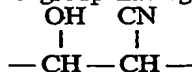
This invention relates to the preparation of saturated aliphatic dicarboxylic acids and monocarboxylic acids.

The object of this invention is to provide 15 an economical and commercially practicable method of manufacturing monobasic and dibasic organic acids. Another object is to provide a method which utilises raw materials which are readily available and relatively inexpensive.

In accordance with this invention, there is provided a process for preparing saturated aliphatic monocarboxylic and dicarboxylic acids characterised by reacting, at a tem- 25 perature at which the reactants are fluid, molten alkali metal hydroxide with a saturated aliphatic carboxylic acid containing 16 to 22 carbon atoms exclusive of the carbon atoms in the cyano or acyloxy substituents 30 specified below, or an ester of said acid and a monohydric or polyhydric alcohol, said acid or ester also containing in its acid chain (a) at least one group having the formula:



in which X is chlorine or bromine and Y is a hydroxy or an —OCOR group in which R is hydrogen or a C_1 — C_5 alkyl group; or 40 (b) at least one group having the formula:

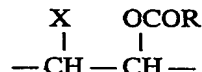


dissolving the resultant mixture of salts in 45 water, and acidifying the resultant aqueous [Price 3/6]

solution to hydrolyse the salts to the acids.

In the above process, the cyano-hydroxy, acyloxy-halo or hydroxy-halo derivatives of a given acid or ester split in essentially the same way, when fused with caustic, to yield 50 ultimately mixtures of essentially the same monocarboxylic and dicarboxylic acids.

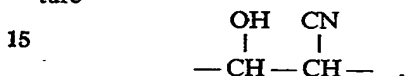
The acyloxy-halo acids and certain of the esters which are employed are themselves the subject of our copending Application No. 55 10538/55 (Serial No. 770,585). Such acids and esters are prepared by reacting an unsaturated aliphatic acid containing 16 to 22 carbon atoms, or an ester thereof, with a 60 *tert*-alkyl hypochlorite or hypobromite—preferably *tert*-butyl hypochlorite—in the presence of a C_1 — C_5 saturated, aliphatic acid such as formic acid or acetic acid. As a result of the reaction, a halogen atom and an acyloxy group are introduced into the 65 chain of the acid on the adjacent carbon atoms which were originally joined by a double bond. Thus, there are introduced into the chains of the acids the groupings having the structure,



in which X is an atom of chlorine or bromine and R is a hydrogen atom or a C_1 — C_5 alkyl 75 group, preferably a methyl group. The unsaturated acids, of which oleic acid is the preferred species, which are thus converted to acyloxy-halo derivatives are typified by oleic, erucic, eleostearic, linoleic, linolenic, 80 clupadonic, palmitoleic and palmitolenic acids, all of which occur in natural oils or fats. The corresponding products, consequently, are the acyloxy-halo-substituted derivatives of palmitic, margaric, stearic, 85 nonadecic, arachidic, eicosic and behenic acids, of which stearic acid is the preferred species.

The cyano-hydroxy acids and certain of the esters which are employed in this process 90

are the subject of our copending Application No. 20095/56 (Serial No. 837,430). Such acids and esters are prepared by reacting an epoxidized aliphatic acid containing 16 to 22 carbon atoms, or an ester thereof, with an alkali metal cyanide. As a result of the reaction, a cyano group and an hydroxyl group are introduced into the chain of the acid on the adjacent carbon atoms which were originally attached to the epoxy group. Thus, there are introduced into the chains of the acids the groupings having the structure



The cyano-hydroxy acids which are subjected to caustic fusion by the process of this invention may, therefore, be the cyano-hydroxy derivatives of palmitic, margaric, stearic, nonadecoic, arachidic, eicosic and behenic acids, of which substituted stearic acid is the preferred species.

The instant invention also embraces the caustic fusion of the esters of the various acids described above as well as of the acids, *per se*. The operable esters are those of the acids and monohydric or polyhydric alcohols which are typified by the following: methyl, ethyl, isopropyl, *n*-butyl, *sec*-butyl, *tert*-butyl, *tert*-amyl, *n*-octyl 2-ethylhexyl, lauryl, octadecyl, cyclohexyl and benzyl alcohols; ethylene glycol, 1,2-propylene glycol, 2-ethylhexandiol-1,3, butandiol-1,3, butandiol-1,4, dodecandiol-1,12; diethylene glycol; glycerol; pentaerythritol; and the isomers and homologues of the above. Since the alcohol portions of the esters do not contribute anything to the formation of acids and are actually destroyed during the caustic fusion, it is preferred to employ the cheapest and most readily available esters of the substituted acids. These are the C_1 - C_4 alkanol esters, i.e. the methyl, ethyl, propyl, and butyl esters, and also the naturally occurring esters. The halo-acylated and cyano-hydroxy glyceridic esters, namely the substituted natural oils and fats, are included in this last category and they are typified by the following halo-acylated and cyano-hydroxy-acylated materials: tallow and soybean, corn, cottonseed, safflower, sunflower, sesame, poppyseed, walnut, peanut, linseed, perilla and sardine oils.

The hydroxy-halo acids and esters which, like the acyloxy-halo acids and esters, are converted by the process of this invention into mixtures of monobasic and dibasic acids are readily prepared, for example, by the alkaline hydrolysis of the acyloxy-halo acids and esters described above.

In a preferred embodiment of the process using as starting material an acyloxy-halo or hydroxy-halo derivative, the starting material is added to the liquid caustic reactant

at a temperature from about 270°C. to about 400°C. In a preferred embodiment of the process using as starting material a cyano-hydroxy derivative, the starting material is added to the liquid caustic at a temperature from about 200°C. to about 400°C. It is much preferred in both cases to employ temperatures from about 310°C. to about 340°C. Alternatively, the caustic and the ester or acid can be mixed and heated together; or the caustic can be added to the heated acid or ester. The addition of water aids in the melting or fusion of the caustic, especially at the lower operating temperatures. As a matter of fact, ordinary commercial grades of sodium and potassium hydroxides contain some water which aids in the fusion of these materials. The important consideration is that the reaction mixture of caustic and the acid or ester be fluid at the temperature of reaction. Obviously the reaction can be carried out at superatmospheric temperatures as well as at atmospheric pressure.

Although the hydroxide of lithium can be used, it is much preferred to employ sodium hydroxide or potassium hydroxide or mixtures of the two for the sake of economy and efficiency.

It is also recommended that an inert liquid such as mineral, e.g. white, oil be present during the caustic fusion reaction. Such a material, although not essential, serves as a flux and greatly facilitates the stirring and mixing of the reactants.

After the caustic fusion the scission products are separated. By the preferred procedure, the cooled reaction mixture, which is usually a soap-like mass, is treated with water in order to dissolve the salts or soaps of the organic acids which have formed. If an organic solvent such as mineral oil has been employed, it is best removed by extraction with a low-boiling organic liquid such as diethyl ether or petroleum ether which is later separated from the high-boiling solvent by distillation. The aqueous solution is then acidified with a strong mineral acid, such as hydrochloric acid or sulfuric acid; and the free organic acids which are thus formed are next removed by extraction with an organic solvent, such as diethyl ether. The organic solvent is stripped off and a mixture of monobasic and polybasic acids is thereby obtained. When it is desired to separate the monobasic and dibasic acids, the crude mixture is dissolved in a dilute solution of a caustic alkali, preferably sodium hydroxide, in an amount sufficient to convert the organic acids to soluble salts. The resultant aqueous solution of salts is mixed with an organic solvent, preferably an inert hydrocarbon such as octane, and the mixture is again acidified with a strong mineral acid to a pH which is

no lower than about 5.5. As a result salts of the monobasic organic acids are converted to the acids *per se*; and these acids are simultaneously extracted by the organic solvent. After removal of the organic solution, the organic monobasic acids are obtained by distillation of the solvent. The aqueous solution is then further acidified to a pH of about 1.5 to 2 and is also preferably cooled to about 5°C. The dibasic acids which then precipitate are filtered off and are washed with water and later dried. This procedure for separating monobasic and dibasic acids is referred to herein as "the pH method".

This process of making monobasic and dibasic acids from hydroxy-halo and acyloxy-halo or cyano-hydroxy acids and esters is very efficient. It is also very economical because the yields of acids are high and the process utilizes derivatives of acids and esters which are themselves easily prepared and hence low in cost.

The following examples, in which all parts are by weight, serve to illustrate the process of this invention.

EXAMPLE 1

Seventy-five parts (1.33 moles) of potassium hydroxide and 53 parts (1.33 moles) of sodium hydroxide were placed in a stainless steel reactor equipped with a detachable cover, stirrer, thermometer and an inlet tube for liquids. The mixture of caustic alkalis was stirred and heated to 330°C. While the temperature was maintained at 320° to 330°, 121 parts (0.33 mole) of a mixture of 9,10- and 10,9-formoxychlorostearic acid (previously made by the reaction of *tert*-butyl hypochlorite and formic acid with oleic acid) was added at a slow uniform rate over a period of approximately two hours. The stirred reaction mixture was heated at 320° to 330°C. for about an hour longer, after which it was allowed to cool to room temperature. The mass of material in the reactor was removed and dissolved in water. The aqueous solution was filtered and was acidified to a pH of 1.5 with a 50% aqueous solution of sulfuric acid. The precipitated acids were filtered off and dried. The product, a mixture of 85 parts of monobasic and dibasic acids, had a neutral equivalent of 141.5. (A neutral equivalent, obtained by titrating a known quantity of an acid or mixture of acids, is a measure of the average molecular weight of the acid for each mole of carboxyl group in the acid or mixture of acids.)

The monobasic and dibasic acids were then separated as follows: The mixture of acids was dissolved in an aqueous solution of sodium hydroxide. To the resultant solution was added 175 parts of octane. This mixture was agitated and heated to 80°C., at which point a 50% aqueous solution of

sulfuric acid was slowly added until the aqueous phase had a pH of 5.9. The organic and aqueous phases were separated. The octane was removed by distillation and a mixture of monobasic acids was obtained as a residue. The aqueous phase was further acidified to a pH of 1.5 and chilled to 5°C. The precipitated mixture of dibasic acids was filtered off, washed and dried. The product, a mixture of 23.6 parts of dibasic acids, 75 had a neutral equivalent of 99 and contained azelaic and sebacic acids.

When the above procedure was repeated with one exception, namely that a reaction temperature 355° to 360°C. was employed, 80 essentially identical results were obtained. Thus, the product was 86 parts of a mixture of monobasic and dibasic acids having a neutral equivalent of 142.

EXAMPLE 2

The procedure described in Example 1 was followed in the caustic fusion of a mixture of 9,10- and 10,9-hydroxychlorostearic acid. To a mixture of 84 parts of sodium hydroxide, 117 parts of potassium hydroxide 90 and 200 parts of mineral oil at 315° to 320°C. there was added slowly 175 parts of a mixture of 9,10- and 10,9-hydroxychlorostearic acid. The reaction mixture was worked up in the manner described above 95 with the exception that the mineral oil was extracted with diethyl ether before the reaction mixture was dissolved in water. A total of 140 parts of a mixture of monobasic and dibasic acids was obtained which had a 100 neutral equivalent of 154. This mixture was found to contain 38 parts of a mixture of dibasic acids, including azelaic and sebacic acids, having a neutral equivalent of 104.

EXAMPLE 3

The procedure of Example 1 was followed 105 in the preparation of a mixture of monobasic and dibasic organic acids from the formoxy-chloro derivative of commercial tallow, which is a glyceridic ester of a mixture of organic acids including oleic and stearic acids. Thus, a mixture of 70 parts (1.25 moles) of potassium hydroxide, 50 parts (1.25 moles) of sodium hydroxide and 150 parts of mineral oil was heated to 325°C. 115 and was held at 320° to 330°C. while to it was added slowly and uniformly, over a period of 50 minutes, 119.5 parts of the chloro-formoxy derivative of tallow. (The last compound was made by the reaction of 120 *tert*-butyl hypochlorite and formic acid with a good commercial grade of tallow.) The reaction mixture was held further for approximately an hour at 325°C. and was then allowed to cool to room temperature, 125 after which it was added to 1000 parts of water. The mineral oil was extracted with 800 parts of ether and was recovered by the subsequent evaporation of the ether. The aqueous solution was acidified to a pH of 130

1.5 and the aqueous phase was extracted with two 600-part portions of diethyl ether. The ether was stripped off and a yield of 96 parts of a mixture of monobasic and dibasic acids having a neutral equivalent of 183 was obtained. These acids were separated by the pH method described above and it was found that the dibasic acids, chiefly azelaic and sebacic acids, constituted approximately 25% of all of the acids formed.

EXAMPLE 4

The procedure described above was followed in the caustic fusion of the formoxy-chloro derivative of another batch of commercial tallow. Thus, 116 parts of the formoxy-chloro tallow was added, over a period of an hour, to a fused mixture of 56 parts of potassium hydroxide, 40 parts of sodium hydroxide, and 150 parts of mineral oil held at 275°C. After the addition, the mixture was held at 275°C. to 280°C. for another hour. The product was treated in the manner described above and a yield of 114.5 parts of mixed acids was obtained, of which approximately 20% were dibasic acids.

EXAMPLE 5

In a similar way, 74 parts of methyl formoxychlorostearate was added over a period of 45 minutes to a mixture of 54 parts of potassium hydroxide, 40 parts of sodium hydroxide and 150 parts of mineral oil at 275° to 280°C. The stirred reaction mixture was held at 275° to 280°C. for an additional period of 40 minutes, after which it was cooled and treated according to the method of Example 3 above. As a result a yield of 60.5 parts of a mixture of monobasic and dibasic acids, having a neutral equivalent of 201, was obtained.

EXAMPLE 6

A mixture of 56 parts of potassium hydroxide, 40 parts of sodium hydroxide and 120 parts of mineral oil was placed in a reactor equipped with a detachable cover, thermometer, stirrer, and an inlet tube for liquids. The stirred mixture was heated to 320° and was held at 320° to 325°C. while to it was added slowly and uniformly over a period of approximately one hour 68 parts of a mixture of 9,10- and 10,9-cyanohydroxystearic acid. (The latter had been made by the reaction of sodium cyanide and epoxy-stearic acid in methanol.) After addition was complete, the stirred reaction mixture was held at 320° to 325°C. for an additional hour. The mass was allowed to cool and was then added to 800 parts of water. The mineral oil was separated and the aqueous phase was extracted with diethyl ether to remove all of the mineral oil. The aqueous phase was then acidified to a pH of 1.5 and the precipitated mixture of acids was extracted by means of diethyl ether. The separated

ether solution was evaporated and a yield of 67 parts of a mixture of acids having a neutral equivalent of 126 was obtained.

The monobasic and dibasic acids were then separated as follows: The mixture of 70 acids was dissolved in an aqueous solution of sodium hydroxide. To the resultant solution was added 100 parts of octane. This mixture was agitated and heated to 80°C., at which point a 50% aqueous solution of 75 sulfuric acid was slowly added until the aqueous phase had a pH of 5.9. The organic and aqueous phases were separated. The octane was removed by distillation and a mixture of monobasic acids was obtained as 80 a residue. The aqueous phase was then further acidified to a pH of 1.5 and chilled to 5°C. The precipitated mixture of dibasic acids was filtered off, washed and dried. The product amounted to 24.6 parts, had a 85 neutral equivalent of 102 and contained azelaic and sebacic acids in essentially equimolar amounts.

This fusion procedure was repeated many times at varying temperatures as low as 90 200°C. and using various grades of cyano-hydroxy-stearic acid derived from varying grades of oleic acid. In all instances the ratio of dibasic acids to monobasic acids was of the order of at least 1 to 2; and in most 95 instances it approached 1 to 1.

As stated above, naturally occurring fats and oils represent a preferred source of the cyano-hydroxy compounds which are converted by the instant process into valuable 100 monobasic and dibasic saturated aliphatic acids. The following examples are typical of the results obtained by the fusion of cyano-hydrins obtained from natural fats and oils.

EXAMPLE 7

A stirred mixture of 73 parts of sodium hydroxide and 120 parts of mineral oil was heated to 275°C. and to it was added, over a period of an hour, 93 parts of methyl cyanohydroxy — "rapeseedate" (i.e. the 110 methyl ester of the cyanohydroxy acids of rapeseed oil containing 3.4% nitrogen). The mixture was heated at 275°C. for an additional half-hour, after which it was treated in the manner described in Example 6. The 115 yield was 87 parts of a mixture of monobasic and dibasic acids having a neutral equivalent of 142. The acids were isolated by the pH method described above and a yield of 19.3 parts of dibasic acids having a neutral 120 equivalent of 108 was obtained.

EXAMPLE 8

The same procedure was employed in the preparation of monobasic and dibasic acids from the caustic fusion of the methyl ester 125 of the cyanohydroxy fatty acids of tallow (containing 1.8% nitrogen). Thus, 69.5 parts of this mixed ester was added dropwise over a period of an hour to a stirred mixture of 56 parts of potassium hydroxide, 40 parts of 130

sodium hydroxide and 120 parts of mineral oil which was held at 255°C. Heating was continued for an additional half-hour. A total of 73 parts of a mixture of acids having a neutral equivalent of 198 was obtained, of which 13.4 parts were dibasic acids having a neutral equivalent of 101.

EXAMPLE 9

The same procedure was followed in the caustic fusion of a glyceridic ester; namely the cyanohydroxy derivative of tallow. Thus, 75 parts of that derivative yielded 75.5 parts of a mixture of acids having a neutral equivalent of 200, of which 13.6 parts were dibasic acids having a neutral equivalent of 101 and including azelaic and sebacic acids.

Essentially the same products were obtained by the fusion of the cyanohydroxy derivative of "brown grease".

Similarly, the fusion of 77.5 parts of the cyanohydroxy acids of tallow gave rise to 77 parts of a mixture of acids having a neutral equivalent of 178, of which 16.8 parts were dibasic acids having a neutral equivalent of 99.5.

The procedure which has been exemplified above is used in the caustic fusion of the cyano-hydroxy, hydroxy-chloro, formoxy-chloro and acetoxy-chloro derivatives of all the aliphatic acids containing 16 to 22 carbon atoms, and also the esters thereof. Obviously, the scission products which are obtained vary depending on the length of the chain of the particular aliphatic acid and also on the position of the cyano-, chloro-, hydroxy, formoxy and acetoxy groups in the acid chains. Furthermore, a mixture of position isomers (e.g. the 9,10- and 10,9-isomers) is invariably obtained in the preparation of the cyano-hydroxy, hydroxy-halo and acyloxy-halo acids and esters and this also gives rise to a mixture of scission products. Consequently, in every case during fusion, a mixture of the salts of both monobasic and dibasic acids is invariably obtained, together with hydrogen and non-acidic scission products which ordinarily pass out of the fusion mixture. The monobasic and dibasic acids are readily separated by the so-called "pH method" described above. The individual acids can be isolated by chromatography; although in many industrial applications—for example in the formation of resins—the mixtures of dibasic acids and mixtures of monobasic acids can be used just about as satisfactorily as the individual acids in the mixtures; and consequently the isolation of the individual acids is not always necessary.

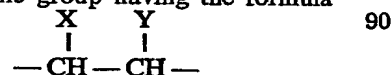
It is to be noted that all of the monobasic and dibasic acids, which are produced in the form of salts during the caustic fusion, can be coprecipitated by means of acid, then isolated as a mixture, thereafter redissolved, and finally separated by the pH method described above. Alternatively, a mixture of all

of the salts resulting from a caustic fusion can, itself, be treated by the pH method of acidulation as a simpler and faster method of separating and isolating the resultant mixture of monobasic acids on the one hand and the mixture of dibasic acids on the other. Obviously, the second procedure eliminates a precipitation step and a redissolving step.

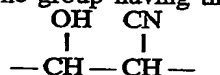
By reason of the provisions contained in Section 9 of the Patents Act, 1949, reference 75 is directed to U.K. Patent No. 706,650.

WHAT WE CLAIM IS:—

1. A process for preparing saturated aliphatic monocarboxylic and dicarboxylic acids characterised by reacting, at a temperature at which the reactants are fluid, molten alkali metal hydroxide with a saturated aliphatic carboxylic acid containing 16 to 22 carbon atoms, exclusive of the carbon atoms in the cyano or acyloxy substituents specified below, or an ester of said acid and a monohydric or polyhydric alcohol, said acid or ester also containing in its acid chain (a) at least one group having the formula



in which X is chlorine or bromine and Y is a hydroxy or an —OCOR group in which R is hydrogen or a C₁—C₈ alkyl group, or (b) at least one group having the formula



dissolving the resultant mixture of salts in water, and acidifying the resultant aqueous solution to hydrolyze the salts to acids.

2. A process according to Claim 1, wherein the alkali metal hydroxide is sodium and/or potassium hydroxide.

3. A process according to Claim 1 or 2, wherein the fusion reaction is carried out in the presence of an inert liquid which serves as a flux for the reactants.

4. A process according to Claim 3, wherein the inert liquid is a mineral oil.

5. A process according to any one of the preceding claims, wherein the product monocarboxylic and dicarboxylic acids are separated from each other by the procedure substantially as hereinbefore described.

6. A process according to any one of the preceding claims, wherein said acid or ester contains at least one hydroxy-halo or acyloxy-halo group and the fusion reaction is carried out at a temperature from about 270°C. to about 400°C.

7. A process according to Claim 6, wherein the fusion reaction is carried out at a temperature of about 310°C. to 340°C.

8. A process according to any one of Claims 1-5, wherein said acid or ester contains at least one cyano-hydroxy group and the fusion reaction is carried out at a temperature from about 200°C. to about 400°C.

9. A process according to Claim 8, wherein the fusion reaction is carried out at a temperature from about 310°C. to about 340°C.
- 5 10. A process according to any one of Claims 1-7, wherein 9,10- or 10,9-chloroformoxy-stearic acid or an ester thereof is used as starting material.
11. A process according to any one of 10 Claims 1-5 or 8 or 9, wherein 9,10- or 10,9-cyano-hydroxystearic acid or an ester thereof is used as starting material.
12. A process according to any one of 15 Claims 1-7, wherein there is used as starting material an acyloxy-halo acid or ester in which the acyloxy group is formoxy or acetoxo.
13. A process according to any one of the preceding claims, wherein there is used as a starting material an ester which is a C₁-C₄ 20 alkanol ester or a glyceridic ester.
14. A process according to Claim 1, when carried out substantially as described in any one of the foregoing Examples.
15. Aliphatic monocarboxylic and dicar- 25 boxylic acids whenever prepared by a method as claimed in any one of the preceding claims or by an obvious chemical equivalent thereof.
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Agents for the Applicants.

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